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The application of CVD diamond films in cyclic voltammetry

R. Torz-Piotrowska [a], A. Wrzyszczyński [a], K. Paprocki [b],
M. Szreiber [b], C. Uniszkiewicz [b], E. Staryga [c,]*
[a] Faculty of Chemical Technology and Engineering, University of Technology
and Life Sciences, ul. Seminaryjna 3, 85-326 Bydgoszcz, Poland
[b] Institute of Physics, Kazimierz Wielki University,
Pl. Weyssenhoffa 11, 85-072 Bydgoszcz, Poland
[c] Institute of Physics, Technical University of Lodz,
ul. Wólczańska 219, 90-924 Łódź, Poland
* Corresponding author: E-mail address: estaryga@p.lodz.pl

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Properties

ABSTRACT

Purpose: The main purpose of these studies was to show the applicability of CVD (Chemical Vapour Deposition) diamond layer in electrochemistry and to work out the technology of manufacturing diamond electrodes.
Design/methodology/approach: The diamond films were deposited on tungsten substrate by HF CVD technique, and then, their quality was checked by Raman spectroscopy. It was shown, using Cyclic Voltammetry (CV) measurements, that un-doped diamond films are chemically stable in aqueous solutions.
Findings: The results of cyclic voltammetry measurements show that diamond electrode on tungsten substrate is electrochemically stable in aqueous solutions over a wide potential range (-3000 mV to 2000 mV). The Raman spectra confirmed the good quality of obtained diamond layer.
Research limitations/implications: In particular, it was shown that diamond electrode showed a wide potential window, very low background current, chemical and physical stability.
Practical implications: Presented results showed that CVD diamond films can find application in production of diamond electrodes for electrochemical application. The sensitivity of CVD diamond layers to the electroactive species indicates on possibility of application of this material for construction of chemical and biological sensors.
Originality/value: The characteristics of diamond electrodes and the resistivity of this material to the chemical attack indicate that it can be employed in a number of electrochemical applications and additionally it can work in harsh environment. The HF CVD diamond layer seems to be the new, promising and versatile material for electrochemical applications.
Keywords: Electrical properties; Diamond films; Working electrode; Cyclic voltammetry

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1. Introduction

One of the main pre-occupation of the research in electrochemistry is continuous development of high-quality and wear resistant electrode material. This type of materials must fulfil specific characteristics such as long-term chemical and electrochemical stability, good electric conductivity, resistance to electrode deactivation and fouling, sufficient mechanical stability, technical feasibility of fabrication and acceptable cost. In the recent past, the electrochemical research focused a lot on anode development in order to improve the electrochemical efficiency of the process. At the beginning, electro-catalytic anodes made of platinum or palladium were developed. This kind of material implies adsorption steps and has high efficiency, but the poisoning of the surface and the wear of the electrode render them less efficient. Discoveries concerning the deposition and the electrochemical properties of synthetic thin films of diamond have opened a new branch of electrochemistry.

The advent of economic methods of preparing polycrystalline diamond via chemical vapour deposition (CVD) has resulted in considerable interest in developing commercial applications for this material [1, 2]. Heat sinks [3, 4], field emitters [5, 6] and electronic devices [7, 8] based on diamond are amongst some of the use that have been proposed. Electrochemistry [9, 10] is presently emerging as an area in which diamond offers distinct advantages over more traditional materials. Indeed devices in which diamond electrodes are an integral component are now being marketed [11, 12]. The first paper on the electrochemistry of boron doped polycrystalline diamond was published by Pleskov et al. [9] in 1987. The demonstration of the possibility of performing electrochemistry on polycrystalline diamond resulted in considerable interest in electrodes fabricated from this new material. Three advantages of diamond electrodes were identified. First, it was demonstrated that diamond electrodes have a large potential window in aqueous solution with low background currents [13-15]. Second, it was shown that electrodes formed from polycrystalline diamond possess physical properties similar to those of bulk diamond [16, 17], including: hardness, resistance to chemical attack (can work in harsh environment), high hole mobility, high thermal conductivity and excellent resistance to radiation damage. Third, the surface is stable and there is little evidence of degradation of electrochemical activity in time [18, 19]. These characteristics of diamond electrodes have been employed in a number of applications. It was demonstrated that the wide potential window at diamond electrodes can be used in the generation of ammonia from aqueous nitrate solutions [20].

The aim of the present work is to show applicability of diamond coated W wire as a new type, low cost working electrode in Cyclic Voltammetry.

2. Experiments

The diamond films were grown via HF CVD method from methyl alcohol vapour (C_3H_3OH) 1 % and hydrogen (99 %). Tungsten filament temperature was established at 2400 K and placed about 6 mm above the substrate. The parameters of growth process were as follows: total pressure in reaction chamber – p = 50 mbar, substrate temperature – 1000 K and working gas flow rate – 100 sccm. Before diamond growth the substrate surfaces were polished mechanically with diamond paste and then cleaned in acetone, methanol and distilled water. Deposition of the polycrystalline diamond film was achieved by activating the gas phase with hot-filaments in the form of coil made of tungsten wire of 0.25 mm in diameter. The deposition time was 16 h, giving a film thickness of approximately 2-4 µm. The scheme of the head of electrode is shown in Fig. 1. The film was allowed to be cooled in the hydrogen atmosphere before removal from the chamber.

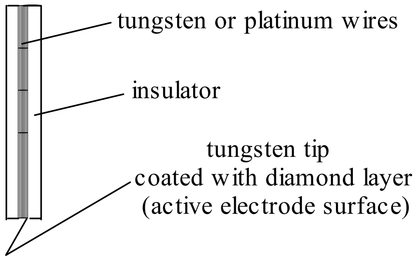

Fig. 1. Scheme of the head of diamond electrode

Before electrochemical studies diamond films were characterised using Raman spectroscopy and scanning electron microscopy (SEM) (JEOL JSM-820).

The Raman spectra were recorded at room temperature in back scattering geometry using Renishaw inVia Raman spectrometer (Renishaw confocal imaging systems). The 488 nm argon laser line was used for excitation.

The electrochemical response of the electrode device was evaluated by Cyclic Voltammetry (CV). Cyclic voltammetric measurements were made with CS-1087 computer - controlled potentiostat (Cypress Systems Inc., Lawrence, KS in a three - electrode configuration. A platinum rod served as the counter electrode and Ag/AgCl (3 M KCl) were used as the reference electrode. De-ionised water was used throughout the experiment and all solutions were deoxygenated with N_2 for at last 15 min prior to measurements.

3. Results and discussion

The quality of the polycrystalline diamond films was analysed using SEM and Raman spectroscopy. SEM image (Fig. 2) shows the film consists of crystals of dimension approximately 1.5 µm and appears continuous wire across the entire substrate.

The Raman spectrum of investigated diamond film, shown in Fig. 3, displays a sharp peak at 1332 cm^{-1} corresponding to sp^3-hybridised carbon. There is no evidence of peaks between 1500 cm^{-1} and 1700 cm^{-1} indicating that the film has a very low graphitic content.

Typical cyclic voltammogram of diamond electrode (W wire coated with diamond) measured in acid solution is presented in Fig. 4. As no other substances are in the solution, which could be electrochemically converted between these potentials, the observed current corresponds to the evolution of hydrogen and oxygen or the formation and consumption of hydrogen and oxygen surface layer. If the hydrogen or oxygen potential is reached, the cathodic and anodic current increases respectively.

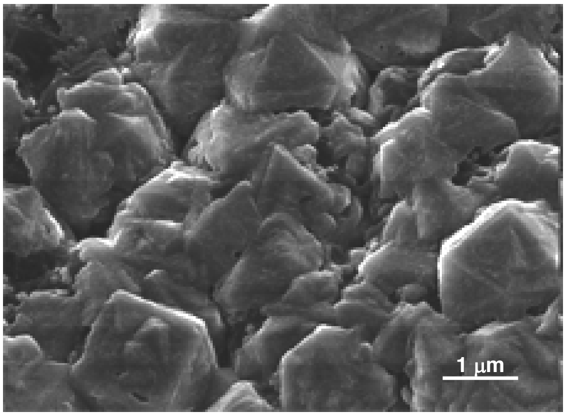

Fig. 2. SEM image of diamond electrode active area

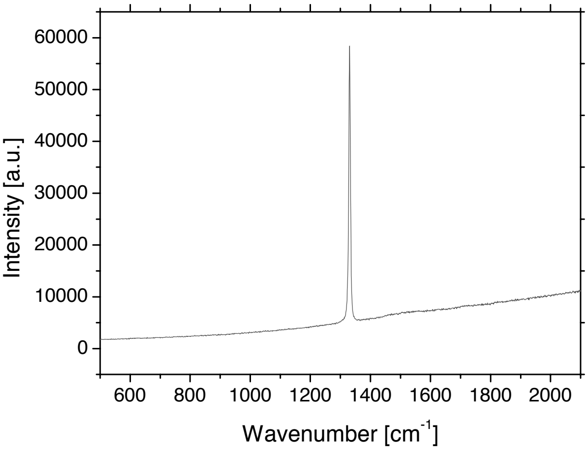

Fig. 3. Raman spectrum of the diamond films shown in SEM image in Fig. 2

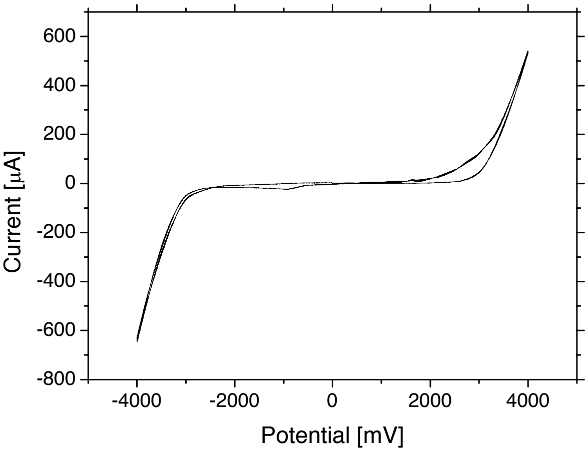

Fig. 4. Cyclic Voltammogram CV curve at diamond electrode in 0.1 M KCl at a scan rate of 0.1 V/s

As one can see in Fig. 4 investigated diamond electrode shows very broad potential window with very low background current. It is also interesting to check behaviour of our electrode in acid solution. In Fig. 5a the anodic current is presented recorded in aqueous solutions of H_2SO_4 at different concentrations. As it was expected, the anodic current should increase as concentration of H_2SO_4 increases. The dependence of I_p vs. concentration (Fig. 5a) shows almost perfect linearity, as it was expected and it means that the electrode works properly.

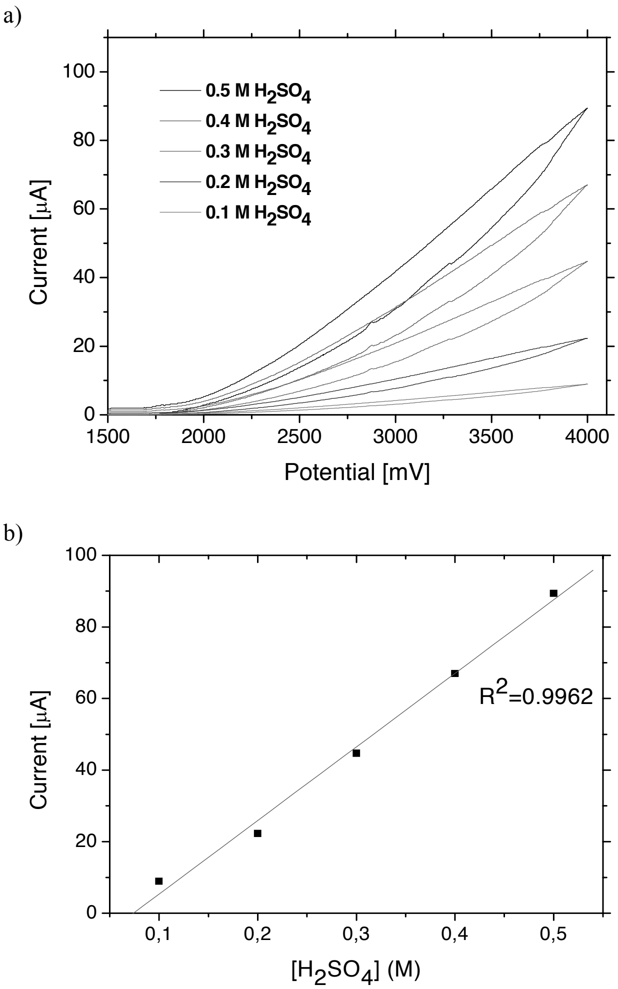

Fig. 5. Anodic current vs. a) potential recorded at different concentration of H_2SO_4 and b) H_2SO_4 concentration

Cyclic voltammetry is the most useful electroanalytical technique for the study of electroactive species and it is often the first experiment performed in electrochemical evolution of electrode surface. Most frequently the electrochemical properties of an electrode are studied using ferric/ferrocyanides in aqueous solution. The voltammetric curves, represented in Fig. 6a were recorded in 0.1 M KCl + 0.01 M $[Fe(CN)_6]^{4-/3-}$ solution at different scan rate.

As it is clearly seen the curves show the symmetrical anodic and cathodic peaks associated with the oxidation and reduction of the ferrocyanide-ferricyanide couple at the diamond - solution interface. The separation between the anodic and cathodic peak (ΔE_p) indicates a degree of reversibility of electrochemical reaction. The electrochemical parameters of diamond electrode obtained from voltammograms presented in Fig. 7a are summarized in Table 1.

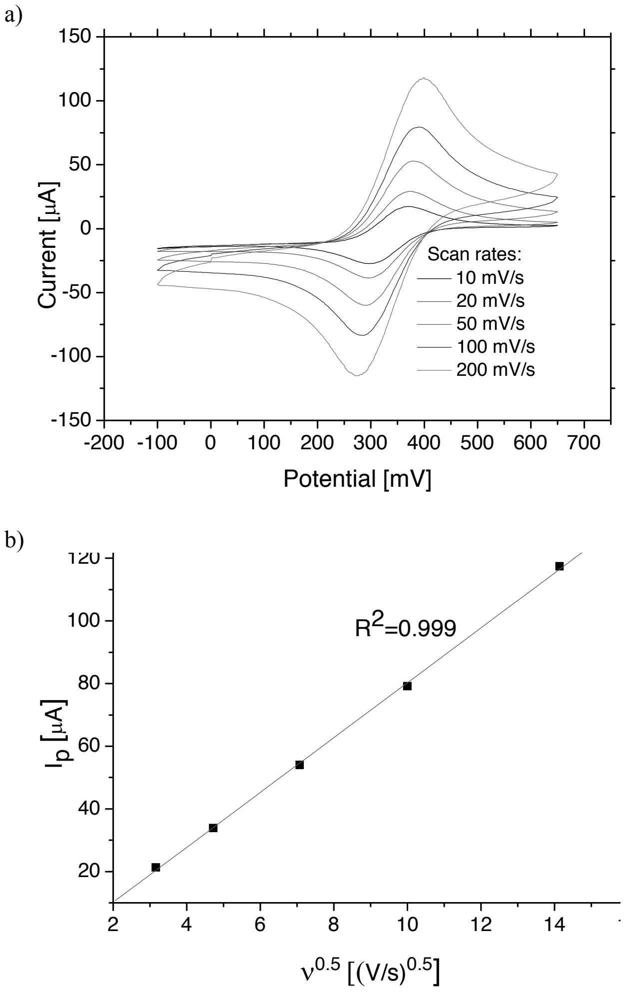

Fig. 6. a) CV curves at diamond electrode in 0.1 M KCl + 0.01 M $[Fe(CN)_6]^{4-/3-}$ at the scan rates v: 10, 20, 50, 100, 200 mV/s; b) peak current I_p vs. the square root of the scan rate ν

The higher the ΔE_p, the more irreversible is the reaction [21, 22]. The results presented in Fig. 6a (ΔE_p are 68-124 mV at a scan rate 10-200 mV/s) indicate the quasi-reversible reaction as expected for diamond electrodes [23, 24]. The anodic to cathodic current peak ratio (I_{pa}/I_{pc}), which is close to 1.0, also indicates that $[Fe\ (CN)_6]^{4-/3-}$ redox reaction on this electrode is quasi-reversible and is not complicated by other side reactions.

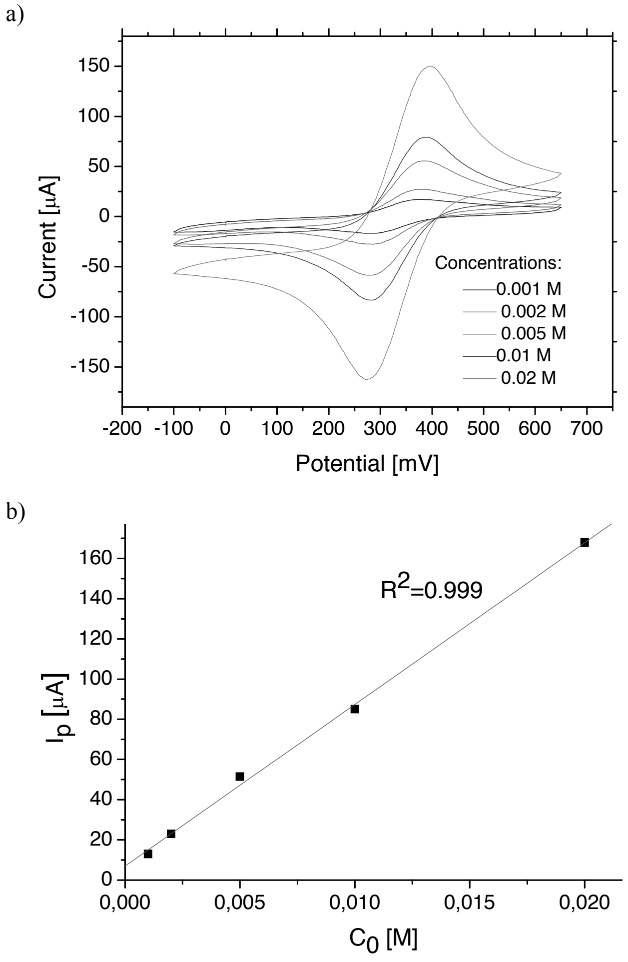

Fig. 7. a) CV curves at diamond electrode at the scan rate of 100 mV/s in 0.1 M KCl containing $[Fe\ (CN)6]^{4-/3-}$ different concentrations (C_0 = 0.001, 0.002, 0.005, 0.01, 0.02 M); b) peak current I_p vs. the concentration C_0 of $[Fe(CN)6]^{3-/4-}$ in 0.1 M KCl

Table 1.
List of peak potentials and currents obtained from CV curves shown in Fig. 5a

υ [mV/s]	E_{pa} [mV]	E_{pc} [mV]	ΔE_p [mV]	I_{pa} [µA]	I_{pc} [µA]	I_{pa}/I_{pc}
10	366	298	68	21.3	23.2	0.92
20	373	295	78	33.9	35.2	0.96
50	380	290	90	54.01	57.06	0.95
100	386	282	104	79.13	82.5	0.96
200	396	272	124	117.4	114.3	1.03

The Fig. 6b shows a plot of the anodic peak against the square root of scan rate. From the slope one can estimate the effective area for diamond electrode according to the Randles-Sevcik equation [9]:

$$I_p = 2.69 \cdot 10^5 \, n^{3/2} D_0^{1/2} v^{1/2} A \, C_0 \,, \qquad (1)$$

where I_p is peak current (A), n = 1 is electron stoichiometry, D_0 is the diffusion coefficient (cm^2/s) for $[Fe(CN)_6]^{4-/3-}$, ν is the scan rate (V/s), A is electrode effective area (cm^2) and C_0 is the bulk concentration in M (mol/cm^3) (C_0 = 0.01 M). The constant is understood to have units ($C\ mol^{-1}\ V^{-1/2}$). Accordingly, equation (1), I_p increased with $\nu^{1/2}$ is directly proportional to concentration.

The voltammetric curves, represented in Fig. 7a were measured in solutions of concentration between 0.001 and 0.02 of $[Fe(CN)_6]^{4-/3-}$ in 0.1M KCl. As it is expected the peak current increases with the concentration increasing of $[Fe(CN)_6]^{4-/3-}$ and the linear relationship is observed between I_p and C_0 (see Fig. 6 and Fig. 7b).

4. Conclusions

In summary diamond film has been deposited on W tungsten wires using HF CVD reactor. As it was confirmed by SEM and Raman spectroscopy the obtained diamond films have very good quality (does not contain graphite-like phase) and it does not show any preferential orientation in respect to substrate surface.

The results of cyclic voltammetry measurements show that diamond electrode on tungsten is electrochemically stable in KCl and H_2SO_4 aqueous electrolytes over a wide potential range (-3000 mV to 2000 mV). The anodic and cathodic peak separation is higher than 59 mV what indicates that electrochemical reactions taking place on diamond surface are of quasireversible character. The peak separation increases with scan rate increase but the ratio of anodic to cathodic peak currents remains almost 1.

The apparent quasi-reversible electrochemical behaviour of the resulting film can be explained mostly by the moderate bulk film resistance. We are now in the process of attempting to obtain more conductive films, while retaining high crystalline quality, by better controlling the substrate temperature to favour lower growth rates.

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